

PATENT ABSTRACTS OF JAPAN

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(21)Application number :	10-255298	(71)Applicant :	MITSUBISHI RAYON CO LTD
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(54) CERAMICS COMPACT AND ITS PRODUCTION**(57)Abstract:**

PROBLEM TO BE SOLVED: To produce a dense ceramics compact consisting essentially of a coal ash, especially a fly ash which is an industrial waste by sintering a coal ash and an inorganic sintering material and imparting a specific bulk density, a specified percentage of water absorption, a specific pore volume and a specified specific surface to the ceramics compact.

SOLUTION: This ceramics compact has 1.0-2.0 g/cm³ bulk density, 0.01-0.8 vol.% percentage of water absorption, 0.01-0.2 cc/g pore volume and 0.1-0.4 m²/g specific surface area. The average particle diameter of a coal ash (e.g. a fly ash) used for producing the compact is 10-40 μ m and the mixing ratio of the coal ash is 60-90 wt.% based on the dry weight. The melting temperature of an inorganic sintering material (e.g. feldspar) is 1,050-1 250°C and the average particle diameter thereof is 0.2-15 μ m. The mixing ratio of the inorganic sintering material is 10-40 wt.% based on the dry weight. When the viscosity of the mixture of the coal ash with the inorganic sintering material is low, an inorganic thickening material (e.g. kaolin) may be used. The mixing ratio thereof is 0-25 wt.% based on the dry weight. The amount of water used is 25-40 pts.wt. based on 100 pts.wt. of the total weight of the coal ash, inorganic sintering material, etc. The heat-treating temperature is 1,000-1,300°C.

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CLAIMS

[Claim(s)]

[Claim 1]A ceramic Plastic solid 0.01 - 0.2 cc/g and whose specific surface area of 1.0-2.0g/cm³ and water absorption 0.01 to 0.8 capacity % and pore volume are [bulk density which coal ash and a minerals sintering material sinter] 0.1-0.4m²/g.

[Claim 2]Coal ash with a mean particle diameter of 10-40 micrometers with dry weight 60 to 90 % of the weight, A minerals sintering material with a mean particle diameter of 0.2-15 micrometers with dry weight with melting temperature of 1050-1250 ** 10 to 40 % of the weight, Minerals thickening material what mixed 0 to 25 % of the weight (the sum total of dry weight of coal ash, a minerals sintering material, and minerals thickening material is made into 100 % of the weight), and water with dry weight, A manufacturing method of the ceramic Plastic solid according to claim 1 heat-treated at 1000-1300 ** after kneading and carrying out extrusion molding and drying, deaerating temporarily at least.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to coal ash especially a ceramic Plastic solid which uses fly ash (fly ash) as the main ingredients, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]Fly ash is a by-product of the particle produced by combustion of coal, especially powdered bituminous coal. Generally fly ash is generated very in large quantities from a coal combustion power plant. Conventionally, disposing by land

processing of reclamation etc. is most, and being effectively used in the form of aggregate for concretes, etc. did not pass over the fly ash of these in part.

[0003]Then, the proposal which is going to use this fly ash effectively came to be made in recent years. For example, in JP,52-78687,A and JP,55-134640,A, the manufacturing method which makes fly ash sinter what mixed and carried out water kneading of a considerable quantity of bentonites which are binders, and obtains a heavy metal capturing material is proposed.

[0004]The art about the ceramic Plastic solid which carried out shaping sintering of the microscopic particles of coal ash is indicated by JP,9-156998,A. however, this art is related with the porous ceramic Plastic solid in which particle diameter has 1-10 micrometers, and the water absorption 10 manufactured using the very small thing - the very high water absorption of 50 capacity % as coal ash of a raw material. By porosity, since intensity is small, such a ceramic Plastic solid has the problem that a use is restricted.

[0005]The coal used in this invention persons' investigation in recent years has much foreign charcoal, and the fly ash by which it is generated from the plant using such foreign charcoal has large particle diameter, Since processes, such as grinding, are needed for adopting the method of JP,9-156998,A, there is a problem of a process becoming complicated or cost going up.

[0006]

[Problem(s) to be Solved by the Invention]Therefore, this invention makes it a technical problem to provide coal ash especially a precise ceramic Plastic solid which uses fly ash as the main ingredients, and a manufacturing method for the same.

[0007]

[Means for Solving the Problem]Bulk density of this invention which coal ash and a minerals sintering material sinter is [1.0-2.0g/cm³ and water absorption] the ceramic Plastic solids 0.01 - 0.2 cc/g and whose specific surface areas 0.01 to 0.8 capacity % and pore volume are 0.1-0.4m²/g.

[0008]Coal ash with a mean particle diameter of 10-40 micrometers this invention with dry weight 60 to 90 % of the weight, A minerals sintering material with a mean particle diameter of 0.2-15 micrometers with dry weight with melting temperature of 1050-1250 ** 10 to 40 % of the weight, Minerals thickening material what mixed 0 to 25 % of the weight (the sum total of dry weight of coal ash, a minerals sintering material, and minerals thickening material is made into 100 % of the weight), and water with dry weight, Deaerating temporarily at least, extrusion molding is kneaded and carried out, and after drying, it is a manufacturing method of the above-mentioned ceramic Plastic solid heat-treated at 1000-1300 **.

[0009]

[Embodiment of the Invention]In 1.0-2.0g/cm³ and water absorption, although 0.01 to 0.8 capacity % and pore volume are [0.01 - 0.2 cc/g and specific surface area] 0.1-0.4m²/g, bulk density the ceramic Plastic solid of this invention, As for 1.1-1.85g/cm³ and desirable water absorption, 0.02 - 0.18 cc/g and the desirable specific surface area of 0.02 to 0.75 capacity % and desirable pore volume are [desirable bulk density] 0.15-0.35m²/g. In this invention, pore volume measures JIS R 2205 and water absorption by JIS R2205, and is measured with a method of mercury penetration, and bulk density measures specific surface area with a BET adsorption method.

[0010]Although the shape in particular of the ceramic Plastic solid of this invention is not

limited, tabular, cylindrical shape, cylindrical shape, a prismatic form, the shape of an rectangular pipe, honeycomb shape, the shape of a star shape, the shape of a clover type, block like shape, or the shape of a ball is preferred.

[0011]The ceramic Plastic solid of this invention is acquired by making coal ash and a minerals sintering material sinter. In order to acquire the ceramic Plastic solid of desired physical properties, the particle diameter of the coal ash of a raw material and a minerals sintering material is chosen suitably.

[0012]The ceramic Plastic solid of this invention The tile for outer walls, the tile block for outer walls, The tile for floors, the tile block for floors, a wallplate, a lightweight aggregate, fire-resistance and building materials for heatproofs, Structural materials, such as heat insulating material, a lightweight aggregate, a roadbed material, a fine aggregate, the paving stone of the yard, the materials for residential-land-development infiltration-of-rain-water layers, It can be used as dumped packing materials, such as materials for horticulture, such as materials for construction, such as a park grand mechanic osmosis structural material, and a road, railroad bed filling material, tree Kiue **, an object for pedestrian deck ****, an object for face-of-slope vegetation spraying and soil for horticulture, a tile, and a tile block, and magnetic Raschig ring.

[0013]Below, the manufacturing method of the ceramic Plastic solid of this invention is explained.

[0014]In the manufacturing method of the ceramic Plastic solid of this invention, minerals thickening material and optimum dose of water are first mixed to coal ash, a minerals sintering material, and arbitration, and a mixture is obtained.

[0015]As for the coal ash used with the manufacturing method of the ceramic Plastic solid of this invention, the mean particle diameter of 10-40 micrometers is a 13-35-micrometer thing preferably. Although fly ash, bottom ash, etc. by which it is generated for example, from a coal combustion power plant etc. as such coal ash are mentioned, especially fly ash is preferred. The mixing ratio of coal ash is 60 to 90 % of the weight in dry weight.

[0016]In the cumulative distribution curve of the volume reference acquired by a laser diffraction type particle-size-distribution measuring method, mean particle diameter is a particle diameter corresponding to 50% in cumulative volume in this invention. Weight % which shows the mixing ratio by this invention means weight % which made the sum total of the dry weight of coal ash, a minerals sintering material, and minerals thickening material 100 % of the weight.

[0017]The minerals sintering material used with the manufacturing method of the ceramic Plastic solid of this invention is 1050-1250 ** in melting temperature. As such a minerals sintering material, coal ash, especially feldspar (melting temperature is nearly 1150 **) with large melting temperature of 1100-1200 ** of fly ash and effect of burying the neighborhood and a cavity part comparatively are preferred.

[0018]0.2-15 micrometers of mean particle diameter of a minerals sintering material are 0.5-5 micrometers preferably. Since the minerals sintering material is bearing the role which buries the cavity part between the particles of coal ash by melting and sintering, selection of the mean particle diameter of a minerals sintering material is important.

[0019]In order that coal ash particles may join together and elaborate mutually by using such a minerals sintering material, the bulk density of the ceramic Plastic solid acquired becomes large, and water absorption, pore volume, and specific surface area become small.

[0020]The mixing ratio of a minerals sintering material is 10 to 40 % of the weight in dry

weight. In order to acquire a more precise ceramic Plastic solid, more ones of the addition rate of a minerals sintering material are preferred, and in order to make small contraction of melting of a minerals sintering material, and the ceramic Plastic solid after heat treatment by sintering, few directions of the addition rate of a minerals sintering material are preferred.

[0021]Only with coal ash and a minerals sintering material, when the viscosity of a mixture is small, in order to improve viscosity and to improve the formability by extrusion molding, minerals thickening material other than coal ash and a minerals sintering material may be used. Although kaolin, bentonite, diatomite, talc, activated clay, etc. are mentioned as such minerals thickening material, bentonite with it is preferred. [especially high thickening property and] [cheap] In dry weight, the mixing ratio of minerals thickening material is 0 to 25 % of the weight, and is 1 to 25 % of the weight preferably. In order to improve viscosity so that it may be easy to fabricate, more ones of the mixing ratio of minerals thickening material are preferred, and in order to lessen adhesion of the Plastic solids after shaping as much as possible, few directions of the addition rate of minerals thickening material are preferred.

[0022]Although the quantity of the water to be used varies with factors, such as a kind of coal ash, a minerals sintering material, and minerals thickening material, it is usually 25 to 40 weight section to total weight 100 weight section of coal ash, a minerals sintering material, and minerals thickening material. In order to lower [that it is easy to fabricate] viscosity like, more ones of the quantity of water are preferred, and in order [which improves the shape retaining property after shaping, and lessens adhesion of Plastic solids as much as possible] to accumulate, few directions of the quantity of water are preferred.

[0023]Even if it adds fine-pores manifestation material, such as inorganic fibers, such as water-soluble thickening material, such as methyl cellulose and hydroxymethylcellulose, glass fiber, and a ceramics fiber, ammonium nitrate, and ammonium carbonate, etc. in addition to the above, it does not interfere with a mixture.

[0024]In this invention, in order to acquire a precise Plastic solid, the inside of the kneading device and extrusion molding apparatus into which the mixture went the mixture in kneading and the process which carries out extrusion molding is deaerated temporarily at least. The pressure at the time of deaeration does not make capability of the pump for deaeration, etc. large more than needed, in order to make predetermined decompression conditions reach for a short time -- 0.1kPa (absolute pressure.) Following abbreviation. The above is preferred, and in order to make smaller contraction of the ceramic Plastic solid by heat treatment by lessening the opening between particles more and obtaining a precise ceramic shaping precursor, it is preferred to carry out by 100 or less kPa.

[0025]Although the kneading machine of continuous system, such as a kneading machine of a batch type, an axial rotation round trip type, a self-cleaning type, etc. which the device in particular used for kneading is not limited, for example, use double arm type agitating blades can be used, a batch type is preferred at the point which can knead while checking the state of a kneading article.

[0026]Although the device in particular used for extrusion molding is not limited, an auger machine type extruding press machine or a piston type extruding press machine is mentioned, for example. The extrusion molding body by which extrusion molding was carried out is suitably cut by suitable length.

[0027]Thus, since ingredients, such as coal ash, a minerals sintering material, and water,

distribute uniformly and the obtained ceramic shaping precursor has a precise structure, there is little contraction of the ceramic Plastic solid at the time of sintering, and its mechanical strength of the ceramic Plastic solid after sintering improves. From such a ceramic shaping precursor, it is effective in a homogeneous ceramic Plastic solid with sufficient reproducibility being acquired.

[0028]A ceramic shaping precursor dries by ranking second, and let it be a dried body of a ceramic shaping precursor. Although a hot-air-drying method, a natural seasoning method, a humidity drying method, etc. which a drying method in particular is not limited, for example, are generally known are mentioned, since the outside surface of a ceramic shaping precursor and an internal drying rate can be brought close, a natural seasoning method and a humidity drying method are preferred.

[0029]Subsequently, heat-treat the dried body of a ceramic shaping precursor, coal ash and a minerals sintering material are made to sinter, and a ceramic Plastic solid is acquired. Heat treatment temperature is usually 1000-1300 **, and is 1120-1250 ** preferably. In order to acquire the ceramic Plastic solid which was more excellent in precision and a mechanical strength, it is preferred to make small the heating rate to heat treatment temperature, and a heating rate is usually 400 **/h or less, and is 100-350 **/h preferably. Since heat treating time changes with heat treatment temperature or mixing ratio of coal ash, it cannot generally say, but it is usually 0.5 to 5 hours.

[0030]

[Example][Example 1] Fly ash 80 spherical weight section with a mean particle diameter of 31 micrometers and feldspar 20 weight section with a mean particle diameter of 6 micrometers were mixed until it became uniform by the double arm type kneader, 32 weight sections of water was added after that, and it kneaded until it became clay-like (material A). Extrusion molding of the obtained kneading article was carried out to 10 mm in thickness, and 95 mm in width with the clay mixing type vacuum extrusion-molding machine under the decompression conditions of 35kPa, it cut in length of 45 mm, and the ceramic shaping precursor was obtained. This was dried for one day in the shade, temperature up was carried out by h in 300 ** /from a room temperature to 1200 **, and heat treatment was performed at 1200 ** for 2 hours. The acquired ceramic Plastic solids are bulk density 1.39g/cm³, water absorption 0.09 capacity %, pore volume 0.09 cc/g, and specific surface area 0.18m²/g.

The ceramic Plastic solid excellent in the mechanical strength was acquired.

When gestalt observation of this ceramic Plastic solid was carried out with the scanning electron microscope, fly ash particles joined mutually together and it checked that most openings between particles were occupied and it had elaborated with feldspar. This ceramic Plastic solid can be used for structural materials, such as a lightweight aggregate, fire-resistance and ***** for heatproofs, and heat insulating material.

[0031][Comparative example 1] In Example 1, except the point of not having performed a vacuum deairing for the material A using the clay mixing type vacuum extrusion-molding machine, extrusion molding, cutting, desiccation, and heat treatment were performed like Example 1, and the ceramic Plastic solid was acquired. Although 0.95 capacity % and pore volume were [0.27 cc/g and the specific surface area of the acquired ceramic Plastic solid] 0.43m²/g, bulk density 1.09g/cm³ and water absorption are inferior, and damage a mechanical strength selectively by few shocks.

[0032][Comparative example 2] In Example 1, the ceramic Plastic solid was manufactured

like Example 1 except the point using coal ash with a mean particle diameter of 88 micrometers which ground bottom ash as coal ash. Although the acquired ceramic Plastic solids were bulk density 1.18g/cm^3 , water absorption 1.29 capacity %, pore volume 0.31 cc/g , and specific surface area $0.31\text{m}^2/\text{g}$, a mechanical strength is inferior and is selectively damaged by few shocks.

[0033][Comparative example 3] In Example 1, fly ash is mixed until it becomes uniform by a double arm type kneader about five weight sections in 95 weight sections and feldspar, Except having kneaded until it added 35 weight sections of water after that and became clay-like, when extrusion molding was performed like Example 1, viscosity and shape retaining property were bad, and the handling after shaping was impossible by adhesion of ceramic shaping precursors, and modification of a ceramic shaping precursor.

[0034][Comparative example 4] The ceramic Plastic solid was manufactured like Example 1 except the point which was 950 ** in heat treatment temperature in Example 1. The acquired ceramic Plastic solid was bulk density 0.92g/cm^3 , water absorption 2.6 capacity %, pore volume [of 0.49cc/g], and specific surface area $0.54\text{m}^2/\text{g}$. The mechanical strength of the ceramic Plastic solid which magnetism-ization does not follow but is selectively damaged also with few shocks was low.

[0035][Comparative example 5] The ceramic Plastic solid was manufactured like Example 1 except the point which was 1350 ** in heat treatment temperature in Example 1. However, the ceramic Plastic solid fused at the time of heat treatment, and not maintaining shape and adjoining ceramic Plastic solids were carrying out melting adherence.

[0036][Example 2] Fly ash 71 spherical weight section with a mean particle diameter of 26 micrometers and feldspar 29 weight section with a mean particle diameter of 6 micrometers were mixed until it became uniform by the double arm type kneader, 37 weight sections of water was added after that, and it kneaded until it became clay-like. Extrusion molding of the obtained kneading article was carried out to the outer diameter of 18 mm, and 12 mm in inside diameter with the clay mixing type vacuum extrusion-molding machine under the decompression conditions of 10kPa, it cut in length of 18 mm, and the Raschig ring-like ceramic shaping precursor was obtained. This was dried for one day in the shade, temperature up was carried out by h in 300 ** /from a room temperature to 1220 **, and heat treatment was performed at 1220 ** for 2 hours. The acquired ceramic Plastic solids are bulk density 1.16g/cm^3 , water absorption 0.05 capacity %, pore volume 0.07 cc/g , and specific surface area $0.16\text{m}^2/\text{g}$.

The ceramic Plastic solid excellent in the mechanical strength was acquired.

When gestalt observation of this ceramic Plastic solid was carried out with the scanning electron microscope, fly ash particles joined mutually together and it checked that most openings between particles were occupied and it had elaborated with feldspar. This ceramic Plastic solid can be used for a dumped packing thing etc. as magnetic Raschig ring.

[0037][Example 3] Fly ash 86 spherical weight section with a mean particle diameter of 29 micrometers and feldspar 14 weight section with a mean particle diameter of 3 micrometers were mixed until it became uniform by the double arm type kneader, 40 weight sections of water was added after that, and it kneaded until it became clay-like. Extrusion molding of the obtained kneading article was carried out to the outer diameter of 1.5 mm with the clay mixing type vacuum extrusion-molding machine under the decompression conditions of 60kPa, it cut in length of 2 mm, and the cylindrical ceramic shaping precursor was obtained. This was dried for one day in the shade, temperature up was carried out by h in 300 ** /

from a room temperature to 1185 **, and heat treatment was performed at 1185 ** for 2 hours. The acquired Plastic solids are bulk density 1.44g/cm³, water absorption 0.17 capacity %, pore volume 0.16 cc/g, and specific surface area 0.34m²/g.

The ceramic Plastic solid excellent in the mechanical strength was acquired.

When gestalt observation of this ceramic Plastic solid was carried out with the scanning electron microscope, fly ash particles joined mutually together and it checked that most openings between particles were occupied and it had elaborated with feldspar. This ceramic Plastic solid can be used as materials for horticulture containing the materials for construction of the paving stone of the yard, the materials for residential-land-development infiltration-of-rain-water layers, a park ground mechanic osmosis structural material, and a road and railroad bed filling material and tree Kiue **, the object for pedestrian deck ****, the object for face-of-slope vegetation spraying, and the soil for horticulture.

[0038][Example 4] Fly ash 78 spherical weight section with a mean particle diameter of 33 micrometers, feldspar 13 weight section with a mean particle diameter of 8 micrometers, and bentonite 9 weight section were mixed until it became uniform by the double arm type kneader, 35 weight sections of water was added after that, and it kneaded until it became clay-like. After carrying out extrusion molding of the obtained kneading article to the outer diameter of 3 mm with the clay mixing type vacuum extrusion-molding machine under the decompression conditions of 7kPa and cutting in length of 3 mm, a spherical ceramic shaping precursor about 3 mm in diameter was obtained for this in tumbling granulator. This was dried for one day in the shade, temperature up was carried out by h in 300 ** / from a room temperature to 1185 **, and heat treatment was performed at 1185 ** for 2 hours. The acquired Plastic solids are bulk density 1.42g/cm³, water absorption 0.04 capacity %, pore volume 0.06 cc/g, and specific surface area 0.22m²/g.

The ceramic Plastic solid excellent in the mechanical strength was acquired.

When gestalt observation of this ceramic Plastic solid was carried out with the scanning electron microscope, fly ash particles joined mutually together and it checked that most openings between particles were occupied and it had elaborated with feldspar. This ceramic Plastic solid can be used as materials for horticulture containing the materials for construction of the paving stone of the yard, the materials for residential-land-development infiltration-of-rain-water layers, a park ground mechanic osmosis structural material, and a road and railroad bed filling material and tree Kiue **, the object for pedestrian deck ****, the object for face-of-slope vegetation spraying, and the soil for horticulture.

[0039]

[Effect of the Invention]According to this invention, the precise ceramic Plastic solid which uses as the main ingredients fly ash which is coal ash, especially industrial waste can be manufactured. The ceramic Plastic solid manufactured by the method of this invention can be used for wide range uses, such as materials for construction, structural materials, materials for horticulture, and dumped packing materials.

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(54) 【発明の名称】 セラミックス成形体およびその製造方法

(57) 【要約】

【課題】 石炭灰、特にフライアッシュを主成分とする緻密なセラミックス成形体、およびその製造方法を提供する。

【解決手段】 石炭灰と無機質焼結材が焼結してなる高密度が1.0~2.0 g/cm³、吸水率が0.01~0.8容量%、細孔容積が0.01~0.2 cc/g、比表面積が0.1~0.4 m²/gであるセラミックス成形体。

【特許請求の範囲】

【請求項1】 石炭灰と無機質焼結材が焼結してなる嵩密度が $1.0 \sim 2.0 \text{ g/cm}^3$ 、吸水率が $0.01 \sim 0.8$ 容量%、細孔容積が $0.01 \sim 0.2 \text{ cc/g}$ 、比表面積が $0.1 \sim 0.4 \text{ m}^2/\text{g}$ であるセラミックス成形体。

【請求項2】 平均粒子径 $10 \sim 40 \mu\text{m}$ の石炭灰が乾燥重量で $60 \sim 90$ 重量%、熔融温度 $1050 \sim 1250^\circ\text{C}$ で平均粒子径 $0.2 \sim 15 \mu\text{m}$ の無機質焼結材が乾燥重量で $10 \sim 40$ 重量%、無機質増粘材が乾燥重量で $0 \sim 25$ 重量%（石炭灰、無機質焼結材および無機質増粘材の乾燥重量の合計を 100 重量%とする）および水を混合したものを、少なくとも一時的に脱気しながら混練りおよび押出成形し、乾燥した後、 $1000 \sim 1300^\circ\text{C}$ で熱処理する請求項1記載のセラミックス成形体の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、石炭灰、特にフライアッシュ（飛散灰）を主成分とするセラミックス成形体、およびその製造方法に関するものである。

【0002】

【従来の技術】フライアッシュは、石炭、特に粉末状の遼青炭の燃焼によって生じる微粒の副産物である。一般にフライアッシュは石炭燃焼動力プラントから極めて大量に生成される。従来これらのフライアッシュは、埋め立て等の陸上処理で処分されることがほとんどで、コンクリート用の骨材等の形で有効に利用されるのは一部に過ぎなかった。

【0003】そこで近年、このフライアッシュを有効に利用しようとする提案がなされるようになった。例えば、特開昭52-78687号公報および特開昭55-134640号公報では、フライアッシュに粘結剤であるベントナイトを相当量混ぜて水練りしたものを焼結させて重金属捕集材を得る製造方法が提案されている。

【0004】また特開平9-156998号公報には石炭灰の微細粒子を成形焼結したセラミックス成形体に関する技術が開示されている。しかしながらこの技術は、原料の石炭灰として粒子径が $1 \sim 10 \mu\text{m}$ と非常に小さいものを用いて製造した吸水率 $10 \sim 50$ 容量%の非常に高い吸水率を有する多孔質のセラミックス成形体に関するものである。このようなセラミックス成形体は、多孔質で強度が小さいので用途が限られるという問題がある。

【0005】また本発明者らの調査では、近年利用される石炭は外国炭が多く、このような外国炭を用いたプラントから発生するフライアッシュは粒子径が大きく、特開平9-156998号公報の方法を採用するには粉碎等の工程が必要になるので、工程が煩雑になったりコストが上昇する等の問題がある。

【0006】

【発明が解決しようとする課題】従って、本発明は石炭灰、特にフライアッシュを主成分とする緻密なセラミックス成形体、およびその製造方法を提供することを課題とする。

【0007】

【課題を解決するための手段】本発明は、石炭灰と無機質焼結材が焼結してなる嵩密度が $1.0 \sim 2.0 \text{ g/cm}^3$ 、吸水率が $0.01 \sim 0.8$ 容量%、細孔容積が $0.01 \sim 0.2 \text{ cc/g}$ 、比表面積が $0.1 \sim 0.4 \text{ m}^2/\text{g}$ であるセラミックス成形体である。

【0008】また本発明は、平均粒子径 $10 \sim 40 \mu\text{m}$ の石炭灰が乾燥重量で $60 \sim 90$ 重量%、熔融温度 $1050 \sim 1250^\circ\text{C}$ で平均粒子径 $0.2 \sim 15 \mu\text{m}$ の無機質焼結材が乾燥重量で $10 \sim 40$ 重量%、無機質増粘材が乾燥重量で $0 \sim 25$ 重量%（石炭灰、無機質焼結材および無機質増粘材の乾燥重量の合計を 100 重量%とする）および水を混合したものを、少なくとも一時的に脱気しながら混練りおよび押出成形し、乾燥した後、 $1000 \sim 1300^\circ\text{C}$ で熱処理する上記セラミックス成形体の製造方法である。

【0009】

【発明の実施の形態】本発明のセラミックス成形体は、嵩密度が $1.0 \sim 2.0 \text{ g/cm}^3$ 、吸水率が $0.01 \sim 0.8$ 容量%、細孔容積が $0.01 \sim 0.2 \text{ cc/g}$ 、比表面積が $0.1 \sim 0.4 \text{ m}^2/\text{g}$ であるが、好ましい嵩密度は $1.1 \sim 1.85 \text{ g/cm}^3$ 、好ましい吸水率は $0.02 \sim 0.75$ 容量%、好ましい細孔容積は $0.02 \sim 0.18 \text{ cc/g}$ 、好ましい比表面積は $0.15 \sim 0.35 \text{ m}^2/\text{g}$ である。尚、本発明において、嵩密度はJIS R 2205、吸水率はJIS R 2205、細孔容積は水銀圧入法、比表面積はBET法により測定する。

【0010】本発明のセラミックス成形体の形状は特に限定されないが、板状、円柱状、円筒状、角柱状、角筒状、ハニカム状、星形状、クローバー形状、ブロック状または球状が好ましい。

【0011】本発明のセラミックス成形体は、石炭灰と無機質焼結材を焼結させて得られたものである。所望の物性のセラミックス成形体を得るために、原料の石炭灰および無機質焼結材の粒径は適宜選択する。

【0012】本発明のセラミックス成形体は、外壁用タイル、外壁用タイルブロック、床用タイル、床用タイルブロック、壁材、軽量骨材、耐火・耐熱用建材、保温材等の建築用資材、軽量骨材、路盤材、細骨材、庭の敷石、宅地造成雨水浸透層用資材、公園グラウンド整備工事浸透構造材料および道路・路床盛土材等の建設用資材、樹木植栽、人工地盤植栽用、のり面植生吹付用および園芸用土壌、タイル、タイルブロック等の園芸用資材、磁性ラッシュヒリング等の不規則充填資材として使用する

ことができる。

【0013】以下に、本発明のセラミックス成形体の製造方法について説明する。

【0014】本発明のセラミックス成形体の製造方法では、まず石炭灰、無機質焼結材、任意に無機質増粘材および適量の水を混合して混合物を得る。

【0015】本発明のセラミックス成形体の製造方法で用いる石炭灰は、平均粒子径10～40 μ m、好ましくは13～35 μ mのものである。このような石炭灰としては例えば、石炭燃焼動力プラント等から発生するフライアッシュ、ボトムアッシュ等が挙げられるが、特にフライアッシュが好ましい。石炭灰の混合割合は、乾燥重量で60～90重量%である。

【0016】本発明で平均粒子径とは、レーザー回折式粒度分布測定法で得られる体積基準の累積分布曲線において、累積体積が50%に対応する粒子直径である。また、本発明で混合割合を示す重量%とは、石炭灰、無機質焼結材および無機質増粘材の乾燥重量の合計を100重量%とした重量%を意味する。

【0017】本発明のセラミックス成形体の製造方法で用いる無機質焼結材は溶融温度が1050～1250 $^{\circ}$ Cのものである。このような無機質焼結材としては、石炭灰、特にフライアッシュの溶融温度1100～1200 $^{\circ}$ Cと比較的近く、空隙部を埋める効果が大きい長石（溶融温度が1150 $^{\circ}$ C近辺）が好ましい。

【0018】また、無機質焼結材の平均粒子径は0.2～15 μ m、好ましくは0.5～5 μ mである。無機質焼結材は溶融および焼結により石炭灰の粒子間の空隙部を埋める役割を担っているため、無機質焼結材の平均粒子径の選択は重要である。

【0019】このような無機質焼結材を使用することで石炭灰粒子が相互に結合および緻密化するため、得られるセラミックス成形体の高密度は大きくなり、吸水率、細孔容積および比表面積は小さくなる。

【0020】無機質焼結材の混合割合は乾燥重量で10～40重量%である。より緻密なセラミックス成形体を得るためには無機質焼結材の添加割合は多い方が好ましく、また無機質焼結材の溶融および焼結による熱処理後のセラミックス成形体の収縮を小さくするためには無機質焼結材の添加割合は少ない方が好ましい。

【0021】また、石炭灰および無機質焼結材だけでは混合物の粘性が小さい場合には、粘性を高めて押出成形による賦型性を高めるために、石炭灰および無機質焼結材の他に無機質増粘材を用いてもよい。このような無機質増粘材としては例えば、カオリン、ベントナイト、ケイソウ土、タルク、活性白土等が挙げられるが、特に増粘性が高く安価なベントナイトが好ましい。無機質増粘材の混合割合は乾燥重量で0～25重量%であり、好ましくは1～25重量%である。成形し易いように粘性を高めるためには無機質増粘材の混合割合は多い方が好ま

しく、成形後の成形体同士の付着をできるだけ少なくするためには、無機質増粘材の添加割合は少ない方が好ましい。

【0022】使用する水の量は石炭灰、無機質焼結材および無機質増粘材の種類等の要因により様々であるが、通常は石炭灰、無機質焼結材および無機質増粘材の合計重量100重量部に対して25～40重量部である。成形し易いように粘性を下げるためには水の量は多い方が好ましく、成形後の保型性を高め、かつ成形体同士の付着をできるだけ少なくするためには水の量は少ない方が好ましい。

【0023】混合物には、上記以外にメチルセルロース、ヒドロキシメチルセルロース等の水溶性増粘材、ガラス繊維、セラミックス繊維等の無機質繊維、硝酸アンモニウム、炭酸アンモニウム等の細孔発現材等を添加しても差し支えない。

【0024】本発明では緻密な成形体を得るために、混合物を混練りおよび押出成形する工程において、混合物の入った混練り装置や押出成形装置の内部を少なくとも一時的に脱気する。脱気時の圧力は、脱気用のポンプ等の能力を必要以上に大きくせず、短時間で所定の減圧条件に到達させるためには0.1kPa（絶対圧、以下省略。）以上が好ましく、粒子間の空隙をより少なくして緻密なセラミックス成形前駆体を得ることで熱処理によるセラミックス成形体の収縮をより小さくするためには100kPa以下で行うことが好ましい。

【0025】混練りに使用する装置は特に限定されず、例えば、双腕型の攪拌羽根を使用するパッチ式の混練り機、軸回転往復式やセルフクリーニング型等の連続式の混練り機等が使用できるが、混練り品の状態を確認しながら混練りを行うことができる点では、パッチ式が好ましい。

【0026】また押出成形に用いる装置は特に限定されないが、例えば、オーガー式押出成形機またはピストン式押出成形機等が挙げられる。押出成形された押出成形体は適当な長さに適宜切断される。

【0027】このようにして得られたセラミックス成形前駆体は、石炭灰、無機質焼結材および水等の成分が均一に分散し、かつ緻密な構造となっているので、焼結時のセラミックス成形体の収縮が少なく、焼結後のセラミックス成形体の機械的強度が向上する。またこのようなセラミックス成形前駆体からは、再現性よく均質なセラミックス成形体が得られるという効果もある。

【0028】セラミックス成形前駆体は次いで乾燥を行いセラミックス成形前駆体の乾燥体とする。乾燥方法は特に限定されず、例えば一般的に知られている熱風乾燥法、自然乾燥法、湿度乾燥法等が挙げられるが、セラミックス成形前駆体の外表面と内部の乾燥速度を近づけることができるので、自然乾燥法および湿度乾燥法が好ましい。

【0029】次いでセラミックス成形前駆体の乾燥体を熱処理し、石炭灰および無機質焼結材を焼結させてセラミックス成形体を得る。熱処理温度は通常1000~1300℃であり、好ましくは1120~1250℃である。より緻密、かつ機械的強度に優れたセラミックス成形体を得るためには、熱処理温度までの昇温速度を小さくすることが好ましく、昇温速度は通常400℃/h以下であり、好ましくは100~350℃/hである。熱処理時間は熱処理温度や石炭灰の混合割合により異なるので一概に言えないが、通常0.5~5時間である。

【0030】

【実施例】【実施例1】平均粒子径31μmの球状のフライアッシュ80重量部および平均粒子径6μmの長石20重量部を双腕式ニーダーにて均一になるまで混合し、その後水を32重量部添加し粘土状になるまで混練りした(材料A)。得られた混練り品を35kPaの減圧条件下にて土練式真空押出し成形機で厚さ10mm、幅95mmに押出し成形し、長さ45mmに切断して、セラミックス成形前駆体を得た。これを1日間日陰で乾燥し、室温から1200℃まで300℃/hで昇温し1200℃で2時間熱処理を行った。得られたセラミックス成形体は、嵩密度1.39g/cm³、吸水率0.09容量%、細孔容積0.09cc/g、比表面積0.18m²/gであり、機械的強度に優れたセラミックス成形体を得られた。このセラミックス成形体を走査型電子顕微鏡にて形態観察したところ、フライアッシュ粒子が相互に結合し、粒子間の空隙の大部分が長石で占められて緻密化していることを確認した。このセラミックス成形体は、軽量骨材、耐火・耐熱用建建材および保温材等の建築用資材に使用できるものであった。

【0031】【比較例1】実施例1において、材料Aを土練式真空押出し成形機を用いて、真空脱気を行わなかった点以外は、実施例1と同様に押出し成形、切断、乾燥および熱処理を行いセラミックス成形体を得た。得られたセラミックス成形体は、嵩密度1.09g/cm³、吸水率が0.95容量%、細孔容積が0.27cc/g、比表面積が0.43m²/gであったが、機械的強度は劣り、僅かな衝撃により部分的に破損するものであった。

【0032】【比較例2】実施例1において、石炭灰としてボトムアッシュを粉砕した平均粒子径88μmの石炭灰を用いた点以外は、実施例1と同様にセラミックス成形体を製造した。得られたセラミックス成形体は、嵩密度1.18g/cm³、吸水率1.29容量%、細孔容積0.31cc/g、比表面積0.31m²/gであったが、機械的強度は劣り、僅かな衝撃により部分的に破損するものであった。

【0033】【比較例3】実施例1において、フライアッシュを95重量部および長石を5重量部を双腕式ニーダーにて均一になるまで混合し、その後水を35重量部

添加し粘土状になるまで混練りした以外は、実施例1と同様に押出し成形を行ったところ、粘性および保型性が悪く、セラミックス成形前駆体同士の付着およびセラミックス成形前駆体の変形により、成形以後の取り扱いが不可能であった。

【0034】【比較例4】実施例1において熱処理温度を950℃とした点以外は、実施例1と同様にセラミックス成形体を製造した。得られたセラミックス成形体は、嵩密度0.92g/cm³、吸水率2.6容量%、細孔容積0.49cc/g、比表面積0.54m²/gであった。また、セラミックス成形体は磁性化が進んでおらず、僅かな衝撃でも部分的に破損する機械的強度の低いものであった。

【0035】【比較例5】実施例1において熱処理温度を1350℃とした点以外は、実施例1と同様にセラミックス成形体を製造した。しかしながら、熱処理時にセラミックス成形体が溶融して形状を維持していないばかりか、隣接するセラミックス成形体同士が溶融固着していた。

【0036】【実施例2】平均粒子径26μmの球状のフライアッシュ71重量部および平均粒子径6μmの長石29重量部を双腕式ニーダーにて均一になるまで混合し、その後水を37重量部添加し粘土状になるまで混練りした。得られた混練り品を10kPaの減圧条件下にて土練式真空押出し成形機で外径18mm、内径12mmに押出し成形し、長さ18mmに切断して、ラッシュリング状のセラミックス成形前駆体を得た。これを1日間日陰で乾燥し、室温から1220℃まで300℃/hで昇温し1220℃で2時間熱処理を行った。得られたセラミックス成形体は、嵩密度1.16g/cm³、吸水率0.05容量%、細孔容積0.07cc/g、比表面積0.16m²/gであり、機械的強度に優れたセラミックス成形体を得られた。このセラミックス成形体を走査型電子顕微鏡にて形態観察したところ、フライアッシュ粒子が相互に結合し、粒子間の空隙の大部分が長石で占められて緻密化していることを確認した。このセラミックス成形体は、磁性ラッシュリングとして不規則充填物等に使用できるものであった。

【0037】【実施例3】平均粒子径29μmの球状のフライアッシュ86重量部および平均粒子径3μmの長石14重量部を双腕式ニーダーにて均一になるまで混合し、その後水を40重量部添加し粘土状になるまで混練りした。得られた混練り品を60kPaの減圧条件下にて土練式真空押出し成形機で外径1.5mmに押出し成形し、長さ2mmに切断して、円柱状のセラミックス成形前駆体を得た。これを1日間日陰で乾燥し、室温から1185℃まで300℃/hで昇温し1185℃で2時間熱処理を行った。得られた成形体は、嵩密度1.44g/cm³、吸水率0.17容量%、細孔容積0.16cc/g、比表面積0.34m²/gであり、機械的強

度に優れたセラミックス成形体を得られた。このセラミックス成形体を走査型電子顕微鏡にて形態観察したところ、フライアッシュ粒子が相互に結合し、粒子間の空隙の大部分が長石で占められて緻密化していることを確認した。このセラミックス成形体は、庭の敷石、宅地造成雨水浸透層用資材、公園グラウンド整備工事浸透構造材料および道路・路床盛土材の建設用資材、並びに樹木植栽、人工地盤植栽用、のり面植生吹付用および園芸用土壌を含む園芸用資材等として使用できるものであった。

【0038】〔実施例4〕平均粒子径 $33\mu\text{m}$ の球状のフライアッシュ78重量部、平均粒子径 $8\mu\text{m}$ の長石13重量部およびベントナイト9重量部を双腕式ニーダーにて均一になるまで混合し、その後水を35重量部添加し粘土状になるまで混練りした。得られた混練り品を 7kPa の減圧条件下にて土練式真空押出し成形機で外径 3mm に押出し成形し、長さ 3mm に切断した後、これを転動造粒機にて直径約 3mm の球状のセラミックス成形前駆体を得た。これを1日間日陰で乾燥し、室温から 1185°C まで 300°C/h で昇温し 1185°C で2時*

*間熱処理を行った。得られた成形体は、嵩密度 1.42g/cm^3 、吸水率 $0.04\text{容量}\%$ 、細孔容積 0.06cc/g 、比表面積 $0.22\text{m}^2/\text{g}$ であり、機械的強度に優れたセラミックス成形体を得られた。このセラミックス成形体を走査型電子顕微鏡にて形態観察したところ、フライアッシュ粒子が相互に結合し、粒子間の空隙の大部分が長石で占められて緻密化していることを確認した。このセラミックス成形体は、庭の敷石、宅地造成雨水浸透層用資材、公園グラウンド整備工事浸透構造材料および道路・路床盛土材の建設用資材、並びに樹木植栽、人工地盤植栽用、のり面植生吹付用および園芸用土壌を含む園芸用資材等として使用できるものであった。

【0039】

【発明の効果】本発明によれば、石炭灰、特に産業廃棄物であるフライアッシュを主成分とする緻密なセラミックス成形体を製造することができる。本発明の方法により製造されたセラミックス成形体は、建設用資材、建築用資材、園芸用資材および不規則充填資材等の広範囲の用途に使用することができるものである。

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